

FINAL DATA REPORT

for

**ANALYSIS OF WATER QUALITY
SAMPLES TAKEN DURING A
NEW YORK BIGHT SURVEY IN JULY 1988**

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and

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1.0 INTRODUCTION

In support of the New York Bight Restoration Plan, Region II of the U.S. Environmental Protection Agency (EPA) conducted a survey from July 5-8, 1988, in the New York Bight to collect water quality samples. The following report presents the results of these analyses. Section 1.0 discusses the objectives and study area of the survey. Section 2.0 describes the collection, processing, and analytical methods. Section 3.0 presents the analytical results and quality control (QC) data.

1.1 OBJECTIVES

Two objectives were accomplished during the survey. The first objective was to collect samples for water quality measurements from selected stations within the Bight. The second objective was to analyze those samples for the following trace metals and nutrients:

1. Total Dissolvable Trace Metals--cadmium (Cd), copper (Cu), nickel (Ni), lead (Pb), zinc (Zn), iron (Fe), and mercury (Hg).
2. Nutrients--total phosphorus (Tot P) total nitrogen (Tot N); total and dissolved orthophosphorus (PO_4); ammonia nitrogen (NH_4), nitrate (NO_3), nitrite (NO_2); and silica (SiO_4).

1.2 STUDY AREA

The study area consisted of three transects (A, B, and C) located in or near the boundaries of the New York Bight. Figure 1 shows the study area and the locations of each transect and associated stations.

Transect A--15 stations circumscribing the entire Bight area from Long Island to Cape May.

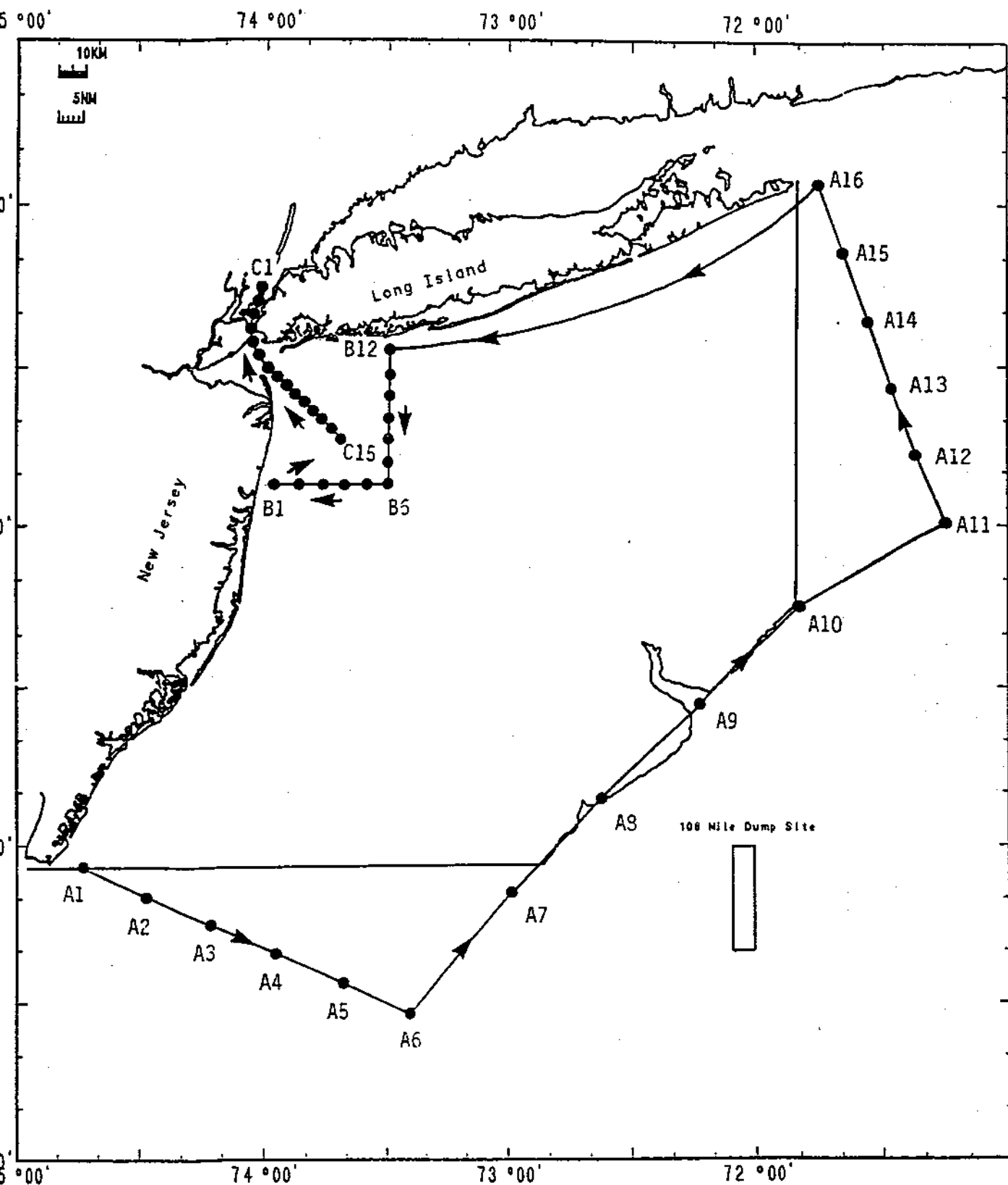


FIGURE 1. STATION LOCATIONS FOR SAMPLES COLLECTED DURING THE NEW YORK BIGHT SURVEY IN JULY 1988.

Transect B--12 stations circumscribing the Apex of the Bight.

Transect C--15 stations extending from Governors Island, New York, through the mouth of the Hudson-Raritan Bay and into the Apex of the Bight.

2.0 SAMPLING AND ANALYTICAL METHODS

Trace metal and nutrient samples were collected at selected stations during the survey. Table 1 summarizes the samples collected for all analytes.

2.1 METHODS FOR COLLECTION AND ANALYSIS OF TRACE METAL SAMPLES

During the survey, 65 samples for analysis of acid-soluble total Cd, Cu, Fe, Ni, Pb, and Zn were collected from 26 selected stations along the three designated transects (A, B, and C). Acid-soluble total metal is defined for these metals as the dissolved and the particulate fraction obtained following acidification of unfiltered samples to a pH of 2. Samples were collected from the surface and pycnocline at 8 stations along Transect A, 6 stations along Transect B, and 12 stations along Transect C (a total of 52 samples). In addition, samples were collected in duplicate from each depth at 5 stations (a total of 12 duplicate samples). One field blank was also collected during the survey.

Samples for acid-soluble total Hg determinations were collected at the same 26 stations sampled for the other trace metals. The Hg samples were composite samples obtained by combining approximately 500 mL from surface seawater and 500 mL from pycnocline seawater into 1-L containers (a total of 26 samples). In addition, one field blank and one duplicate were collected. Acid-soluble total dissolvable Hg is defined here as the dissolved metal and the particulate fraction obtained following acidification of the unfiltered sample to a pH of 1.

TABLE 1. SUMMARY OF THE SAMPLES COLLECTED DURING THE NEW YORK BIGHT WATER QUALITY SURVEY

Analyte	Samples				Total
	Surface	Subpycnocline	Blanks	Other QC	
Trace Metals	26	26	1	12	65
Mercury ^a	26	--	1	1	28
Nutrients	39	3	-	0	78

^aSurface and pycnocline samples composited into a single sample.

Samples for total trace metals (Cd, Ni, Cu, Pb, Zn, Fe, and Hg) were collected and processed according to EPA standard operating procedures (SOPs 5-01 and 6-01) prepared by Battelle for EPA under the 106-Mile Site monitoring program (Battelle, 1987a). Stations were sampled using GO-FLO bottles. Aliquots were then transferred to Teflon containers for subsequent Hg determinations, and to polyethylene containers for the remaining trace metals. Each 1-L Hg sample was acidified with 5 mL high-purity nitric acid. The samples collected for the other metals were acidified with 1 mL nitric acid per liter of sample.

Hg samples were analyzed in accordance with SOP 4-55 (Battelle, 1987b). The other trace metal samples were analyzed in accordance with SOP 4-53 (Battelle, 1987b). The analytical requirements for all targeted analytes are presented in Table 2. To verify precision and accuracy of analytical measurements, a number of quality control samples were analyzed. Precision (expressed as relative percent difference) was estimated from the variation in the results of duplicate samples. Analytical accuracy was determined from standard reference materials (when available), from a matrix spiking exercise, or both and expressed as percent recovery in each case.

2.2 METHODS FOR COLLECTION AND ANALYSIS OF NUTRIENT SAMPLES

Seventy-eight dissolved and total nutrient samples were collected at 39 stations along the three transects: 16 stations along Transect A, 11 stations along Transect B, and 12 stations along Transect C. At each station samples were collected from two depths, the surface and the pycnocline. Three 20-mL subsamples were collected from each sample; two were filtered for analysis of dissolved nutrients, and the unfiltered sample was analyzed for total nitrogen and phosphorus.

Samples for dissolved (PO_4 , NH_4 , NO_3 , NO_2 , and SiO_4) and total nutrients were collected in accordance with SOP 6-01 (Battelle, 1987a). For the dissolved fraction, two 20-mL subsamples were filtered into polyethylene bottles and stored

TABLE 2. SUMMARY OF THE DATA REQUIREMENTS FOR SEAWATER SAMPLES COLLECTED IN THE NEW YORK BIGHT

Parameter	Units	Detection Limit	Accuracy	Precision	Method
Seawater Metals					
Hg	µg/L	0.0002	50	30	Gold amalgamation, Hg analyzer
Cd, Zn, Cu, Pb	µg/L	0.005	50	30	Chelation-extraction, GFAA
Fe, Ni	µg/L	0.050	50	30	Chelation-extraction, GFAA
Nutrients^a					
Total Phosphorus	µmol/L	0.08	30	10	3-channel Technicon auto analyzer
	µg/L	2.5			
Total Nitrogen	µmol/L	2.5	30	10	3-channel Technicon auto analyzer
	µg/L	6.0			
NH ₄ -Nb	µmol/L	0.08	30	10	3-channel Technicon auto analyzer
	µg/L	1.1			
NO ₃ -Nb	µmol/L	0.04	30	10	3-channel Technicon auto analyzer
	µg/L	0.5			
NO ₂ O-Nb	µmol/L	0.02	30	10	3-channel Technicon auto analyzer
	µg/L	0.3			
PO ₄ -Pc	µmol/L	0.02	30	10	3-channel Technicon auto analyzer
	µg/L	0.6			
SiO ₂ -S _{id}	µmol/L	0.08	30	10	3-channel Technicon auto analyzer
	µg/L	2.2			

^aDetection limits for nutrients = 2x standard deviation for triplicate analysis of standards.

^bDetection limits for nitrogen containing NO₂, NO₃, NH₄ reported as µg/L of N.

^cDetection limits for phosphates containing PO₄ reported as µg/L of P.

^dDetection limits for silica containing SiO₂ reported as µg/L of Si.

frozen until analysis. For the total fraction, one 20-mL unfiltered subsample was stored frozen in polyethylene bottles until analysis.

These samples were subsequently processed and analyzed according to the protocol entitled "Automated Analysis of Nutrients in Seawater: A Manual of Techniques" (Appendix A). Analytical requirements for the targeted nutrients are presented in Table 2.

3.0 RESULTS

The analytical results for all samples collected during the New York Bight Survey (July 1988) are presented in Appendices B, C and D.

3.1 TRACE METALS

3.1.1 Analytical Results

All Hg data are presented in Table B-1 of Appendix B. Only general conclusions can be drawn from these Hg data, because surface and pycnocline aliquots were combined to form a single Hg sample.

The concentrations of Cd, Cu, Fe, Ni, Pb and Zn determined from New York Bight samples are tabulated in Appendix C (Table C-1). In general, the consistency the data set for metals indicates a contamination-free sampling effort.

3.1.2 QUALITY CONTROL ANALYSIS

Tables 3 and 4 list the method detection limits and contribution of metals to the analytical results from the procedural blanks. All field samples contained metal concentrations that were well above the method detection limits for all metals determined. The metal data have been corrected for

TABLE 3. METHOD DETECTION LIMITS ($\mu\text{g/L}$) FOR ANALYSIS OF METALS IN SAMPLES COLLECTED FROM THE NEW YORK BIGHT IN JULY 1988

Cd	Cu	Fe	Ni	Pb	Zn	Hg
0.002	0.03	0.10	0.02	0.004	0.01	0.00015

TABLE 4. ANAYTE CONTENT ($\mu\text{g/L}$) IN THE PROCEDURAL BLANKS ASSOICATED WITH THE SAMPLES COLLECTED FROM THE NEW YORK BIGHT IN JULY 1988

Sample ID	Cda	Cua	Fea	Nia	Pba	Zna	Hgb
GI52-PB	0.016	0.09	2.37	7.89	0.013	0.09	
GI53-PB	0.016	0.18	1.90	8.06	0.013	0.09	
GI56-PB	0.005	<.02	0.13	0.06	<.003	0.02	
GI57-PB	0.005	<.02	0.13	0.04	<.003	0.02	
GI48-PB	0.005	<.01	<.10	<.02	0.004	0.01	
GI49-PB	0.005	<.01	<.10	<.02	<.004	0.07	
GH66-AB	-	-	-	-	-	-	0.000790
GH67-AB	-	-	-	-	-	-	0.000694
GH72-AB	-	-	-	-	-	-	0.000238
GH73-AB	-	-	-	-	-	-	0.000266
GH88-AB	-	-	-	-	-	-	0.000362
GH89-AB	-	-	-	-	-	-	0.000322
GH94-AB	-	-	-	-	-	-	0.000092
GI01-AB	-	-	-	-	-	-	0.000022
GI02-AB	-	-	-	-	-	-	0.000002

aCalculated using an extract volume of 2 mL and a sample volume of 200 mL.

bCalculated using a sample volume of 500 mL.

blanks where the analyte blank concentrations were consistent within a processing batch. All of the metal data generated met the precision and accuracy criteria outlined in Table 2, with the exception of the duplicate Hg analyses (Tables B-2 and 3,; C-2, 3, and 4). The Hg precision results were determined to be 31 and 36 (RPD), falling outside of the specified limit of 30 percent. Two of ten blank samples spiked with a known amount of Hg fell outside of the 50 percent recovery criterion. The two field samples spiked with Hg resulted in recoveries of 53 and 73 percent.

3.2 NUTRIENTS

Results for all nutrient samples collected during the survey are presented in Table D-1 of Appendix D. Concentrations of NH_4 , NO_3 , and PO_4 from unfiltered samples were not required. However, because the analyses were performed and the data are available, the values are reported. All nutrient values are reported in micromoles per liter (μM).

The nitrate data from filtered samples for Transects A and B indicate that many of the filtered samples may have been contaminated during filtration. The values for NO_3 are considerably higher (in some cases an order of magnitude or greater) than those for Total N analyzed from the unfiltered samples. High NO_3 concentrations may have been caused by cross contamination from nitric acid used in processing the trace metal samples. Dissolved nitrate values can be estimated for the contaminated samples by using the NO_3 results from the unfiltered fraction if it is understood that some of the NO_3 may be contributed by the particulate fraction.

The ammonia data from Transects A and B indicate that some of the samples (filtered and unfiltered) may have been contaminated or that some of the ammonia may have volatilized from the samples during processing and analysis. Although filtered samples collected along Transects A and B appear to be contaminated with NO_3 and NH_4^+ , those collected along Transect C show no evidence of contamination. In addition, contamination from the other

dissolved and total nutrient parameters is not evident in any of the samples collected along Transects A, B, and C. This data set, with the exception of NO_3 and NH_4^+ , falls within the quality control guidelines described in the protocol in Appendix A.

4.0 REFERENCES

- Battelle. 1987a. Quality Assurance/Quality Control (QA/QC) Document for the 106-Mile Deepwater Dumpsite Monitoring Program. A report submitted to the U.S. Environmental Protection Agency under Contract No. 68-03-3319. Work Assignment 45.
- Battelle. 1987b. Sampling and Analytical Procedures for the Ocean Incineration Research Burn Program (RBSA Plans) Volumes I and II. A report submitted to the U.S. Environmental Protection Agency under Contract No. 68-03-3319. Work Assignment 10.

APPENDIX A

AUTOMATED ANALYSIS OF NUTRIENTS IN SEAWATER:
A MANUAL OF TECHNIQUES

Provided by Dr. Theodore C. Loder
of the University of New Hampshire

AUTOMATED ANALYSIS OF NUTRIENTS IN SEAWATER:
A MANUAL OF TECHNIQUES

by

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June 1977

TECHNICAL REPORT

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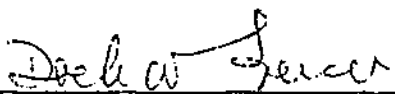

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I.

INTRODUCTION

This manual is written for the person who has some familiarity with the principles of automated chemistry. A few of the principles will be repeated here, but for a more complete treatment of the topic the reader is referred to the following articles: Technicon Industrial Systems, Manual TNO-0210-00 (1970) and Snyder et al. (1976).

The fundamental feature of continuous flow automated chemistry is the segmentation of the flow stream of samples and reagents with small bubbles of air. The bubbles serve three primary purposes. First, the bubbles in the fluid stream cause friction with the tubing, creating turbulent rather than laminar flow; this keeps the liquids well mixed. Second, the bubbles keep each sample separated from the next. Finally, the bubbles continually scrub the walls of the tubing, thus removing any traces of material adhering to the walls.

A second feature of continuous flow automated chemistry is that all operational conditions are systematically maintained the same. Thus, each sample is subjected to exactly the same quantity of reagents, the same temperature, and the same mixing time as every other sample and standard. This, therefore, eliminates the necessity to have reactions go to completion, although many reactions do. This approach will not decrease reliability or substantially affect the sensitivity, as each recorded result represents the sum of the measurements of a large number of analyses performed on each sample. Thus, although a steady-state completed reaction may not be achieved, each sample is repeatedly measured at some constant percentage of steady-state.

This manual is intended to document the methods in use by the University of New Hampshire and Woods Hole Oceanographic Institution at the time of this writing. It describes what the authors feel are the most sensitive and reliable methods for the commonly determined nutrients in seawater, and the problems associated with each method.

The authors thank Gordon Smith (University of New Hampshire) for his assistance in the preparation of this manual, and Roger Shepherd (Duke Marine Laboratory) for teaching us the problems of operating an Auto-Analyzer at sea.

II.

NUTRIENT METHODS

1. PHOSPHATE

The basic method is Technicon Industrial Method No. 155-71W (1973), which is a modification of the Murphy and Riley (1962) single solution method. The method depends on the formation of a phosphomolybdate blue complex, the color of which is read at a wavelength of 880 nm.

Below are described the reagents used in the phosphate system. All reagents should be ACS grade; all water should be distilled and deionized (DDW). DDW is also used as Sampler IV wash water and in setting Auto-Analyzer baseline. We find a reagent blank absorbance ranging from 0.01 to 0.02 using DDW as a sample (see Section III - 3).

4.9N H₂SO₄: Add 136 ml conc H₂SO₄ to 800 ml DDW; after cooling dilute to one liter.

ultra-wet

Diluent Water: Add 1.0 ml Wetting Agent A (Technicon No. T01-0214) to one liter DDW just before use. We recommend you do not use Levor IV as a wetting agent even though it is recommended by Technicon.

Ammonium Molybdate: Dissolve 40g ammonium molybdate in one liter DDW. Stable for several weeks.

Antimony Potassium Tartrate: Dissolve 0.75g antimony potassium tartrate in 250 ml DDW. Stable for several months.

Mixed Reagent: Dissolve 0.648 g ascorbic acid in 36 ml DDW; add 60 ml 4.9N H₂SO₄, 18 ml ammonium molybdate solution and 6 ml antimony potassium tartrate solution. Keep in amber bottle and use within 8 hrs. Makes 120 ml reagent, which is adequate for 8 hrs at a consumption rate of 13.8 ml/hr.

The flow diagram for the system is shown in Figure 1.

Some operational notes for this method are summarized below.

- A 40/hr 1:1 cam gives good, reproducible results
- The colorimeter phototubes must be S-1 (Technicon No. 199-B021-04)
- The colorimeter must be in the Damp I mode
- For routine analysis a STD CAL of 8.00 is used, giving a full scale value of approximately 5.00 $\mu\text{g at/l}$
- For a discussion of calibration and blank problems refer to Sections III 2-3
- 0.1 N NaOH should be used for 5 min at the beginning of set-up to clean out system

PHOSPHATE

116-D221-01

STD CAL 5.00

RANGE 0-5 μg at/l

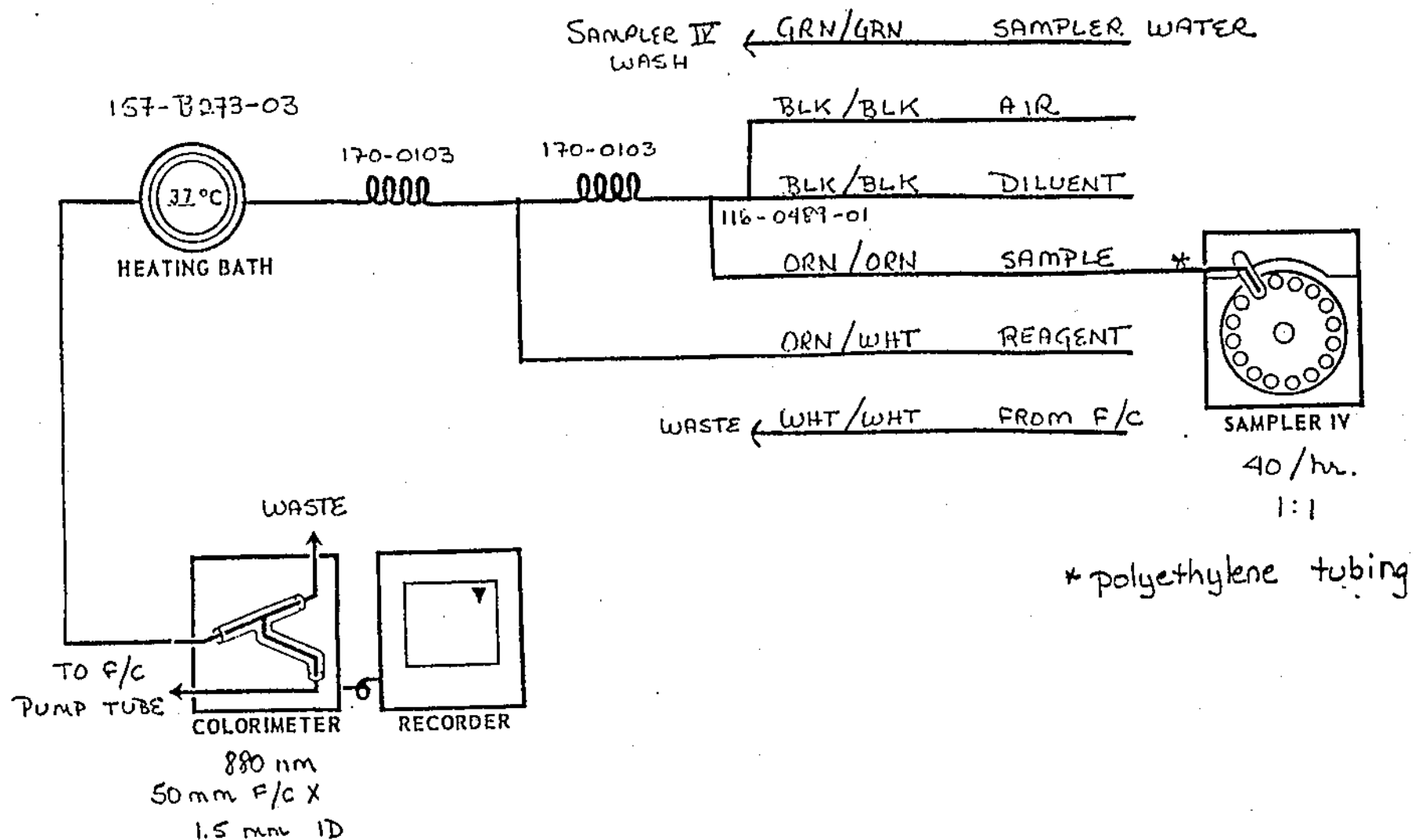


Figure 1. Flow diagram for automated analysis of phosphate in seawater.

II.

2. SILICATE

The method is basically Technicon Industrial Method No. 186-72W (1973). The method involves the formation of a silicomolybdate blue complex, which is analyzed colorimetrically at a wavelength of 660 nm.

Below are described the reagents used in the silicate system. All reagents should be ACS grade; all water should be distilled and deionized (DDW). DDW is also used as Sampler IV wash water and in setting Auto-Analyzer baseline. We find a reagent blank absorbance ranging from 0.01 to 0.02 using DDW as a sample.

Ammonium Molybdate: Dissolve 10g ammonium molybdate in one liter 0.1 N H_2SO_4 (prepare by diluting 2.8 ml conc H_2SO_4 to one liter with DDW). Stable for several weeks if stored in amber plastic. Should be discarded if any precipitate forms in the solution. 60
412

Oxalic Acid: Dissolve 50g oxalic acid and dilute to one liter with DDW. Stable for many months. 66
20-1/1

Ascorbic Acid: Dissolve 17.6 g ascorbic acid in DDW containing 50 ml acetone; dilute to one liter with DDW. Add 0.5 ml Levor IV Wetting Agent (Technicon No. T21-0332). Stable for several weeks if refrigerated. 60
412
25-1/1

The flow diagram for the system is shown in Figure 2.

Some operational notes for this method are summarized below.

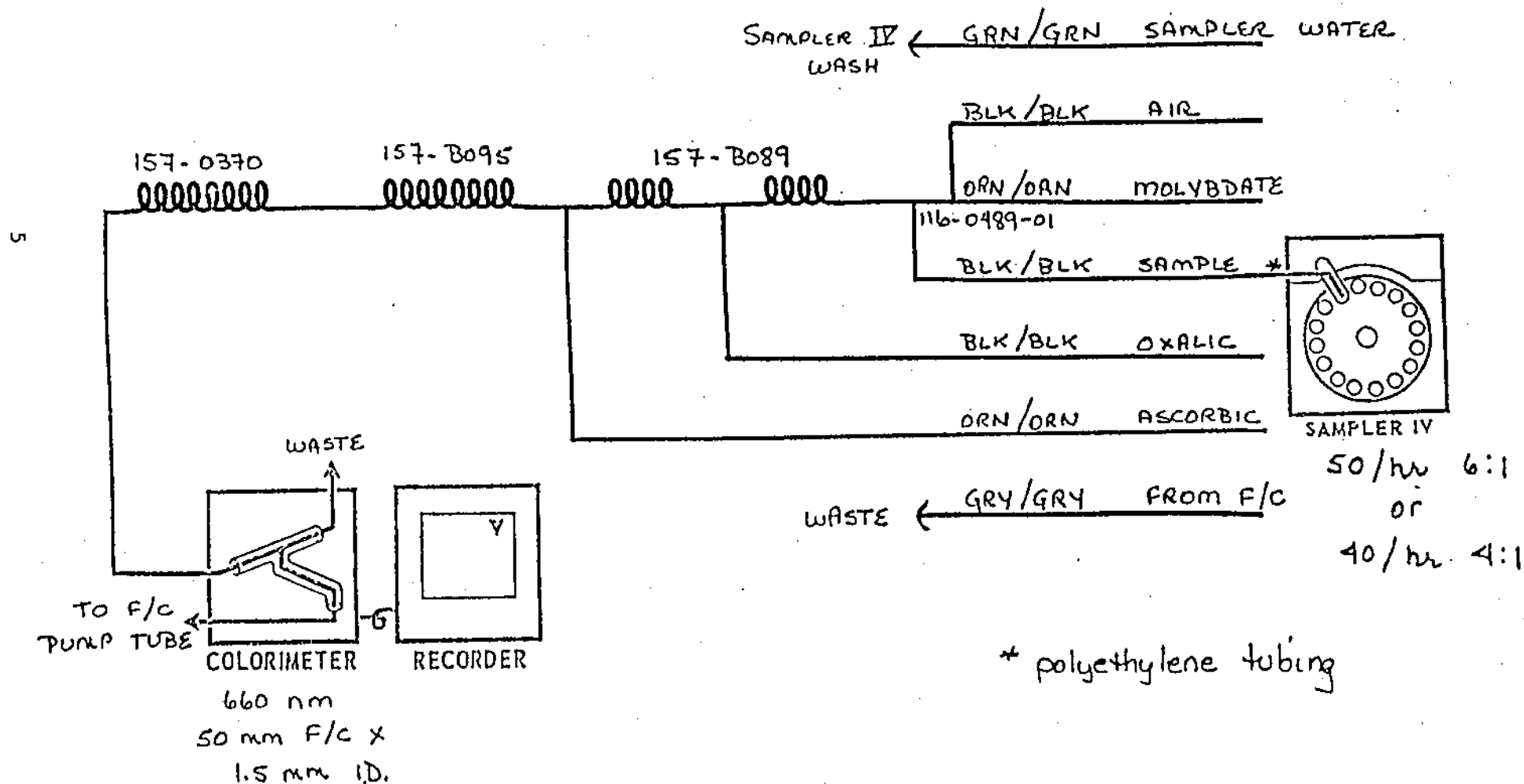
- a. All volumetrics used for standards should be made of linear polyethylene, to avoid contamination by leaching from the glass.
- b. When analyzing only silicate or silicate in combination with nitrite a 50/hr 6:1 cam should be used; when analyzing in combination with any other nutrient a 40/hr 1:1 cam is recommended.
- c. The colorimeter phototubes must be S-1 (Technicon No. 199-B021-04).
- d. The colorimeter must be in the Damp 1 mode.
- e. For routine analysis a STD CAL of 5.00 is used, giving a full scale value of approximately 50 μg at/l.
- f. For a discussion of calibration and blank problems refer to Sections III 2-3.
- g. This is one reaction that does not go to completion; the degree of completion is temperature sensitive. Thus, care should be taken to ensure that a given set of samples are analyzed under similar laboratory temperatures.

SILICATE

116-D291-01

STD CAL 5.00

RANGE 0-50 μg at 1 ℓ



II.

3. NITRATE & NITRITE

The basic method for this analysis is Technicon Industrial Method No. 158-71W/Tentative (1972), which utilizes copper-cadmium reduction of nitrate to nitrite with NH_4Cl as a buffer. For a discussion of the problems associated with EDTA as the buffer choice (Brewer & Riley, 1965) refer to Glibert & Mlodzinska (1977).

Below are described the reagents in use in the nitrate system. All reagents should be ACS grade; all water should be distilled and deionized (DDW). DDW is also used as Sampler IV wash water and in setting Auto-Analyzer baseline. We find a reagent blank absorbance ranging from 0.02 to 0.04 using DDW as a sample with the column in line.

Ammonium Chloride: Dissolve 10g NH_4Cl and 3-4 pellets NaOH in one liter of DDW. Stable for several months if refrigerated.

Color Reagent: Dissolve 10g sulfanilamide and 0.5g N-1-naphthylethylene diamine dihydrochloride to one liter with 10% phosphoric acid. Add 0.5 ml Brij-35 (Technicon No. T21-0110). Stable for one month if refrigerated.

Cadmium Powder: Clean with concentrated HCl, rinse well (10-20 times) with DDW. Treat cadmium with 2% w/v copper sulfate; swirl the mixture until no blue color remains. Wash thoroughly with DDW (10-20 times). Transfer the treated cadmium to a glass column using an eye-dropper or Pasteur pipette. Insert a glass wool plug at each end of the column.

The flow diagram for the nitrate and nitrite system is shown in Figure 3.

Some operational notes for this method are summarized below:

- a) A 4-way valve (Hamilton Syringe Co. No. 4mmmm4 (ML3300) inserted just before the cadmium column greatly facilitates set-up and helps eliminate air bubbles in the column.
- b) A 40/hr 1:1 cam gives best results.
- c) The colorimeter phototubes must be S-10 (Technicon No. 199-B021-01).
- d) The operational STD CAL will depend on the age and efficiency of the column. For a new column a STD CAL of 3.00 gives a full scale value of approximately 20 μg at/l.
- e) For a discussion of calibration and blank problems refer to Sections III 2-3.
- f) When analyzing pore water samples, or samples with either a high sulfide or high organic content, the following procedure is recommended. A short column (3 cm or longer) of activated charcoal

II.

3. NITRATE & NITRITE (Continued)

or of Amberlite ion-exchange resin XAD-4 is inserted just before the cadmium column in the cartridge. This will eliminate the organics without affecting the nitrate concentration. The charcoal or resin may be fitted into a piece of purple-white pump tubing, which may be cut to the desired length. The type of samples will determine what length column will be necessary, and whether the charcoal or resin will work better. Slight smearing of the peaks may be expected with this procedure. When analyzing samples with this method it is best to run standards after every 3-4 samples, and to run at least duplicates on each sample.

NITRATE & NITRITE

116 - D233 - 01

STD CAL 3.00

RANGE 0 - 20 $\mu\text{g at/l}$

SAMPLER IV ← GRN / GRN SAMPLER WATER
WASH

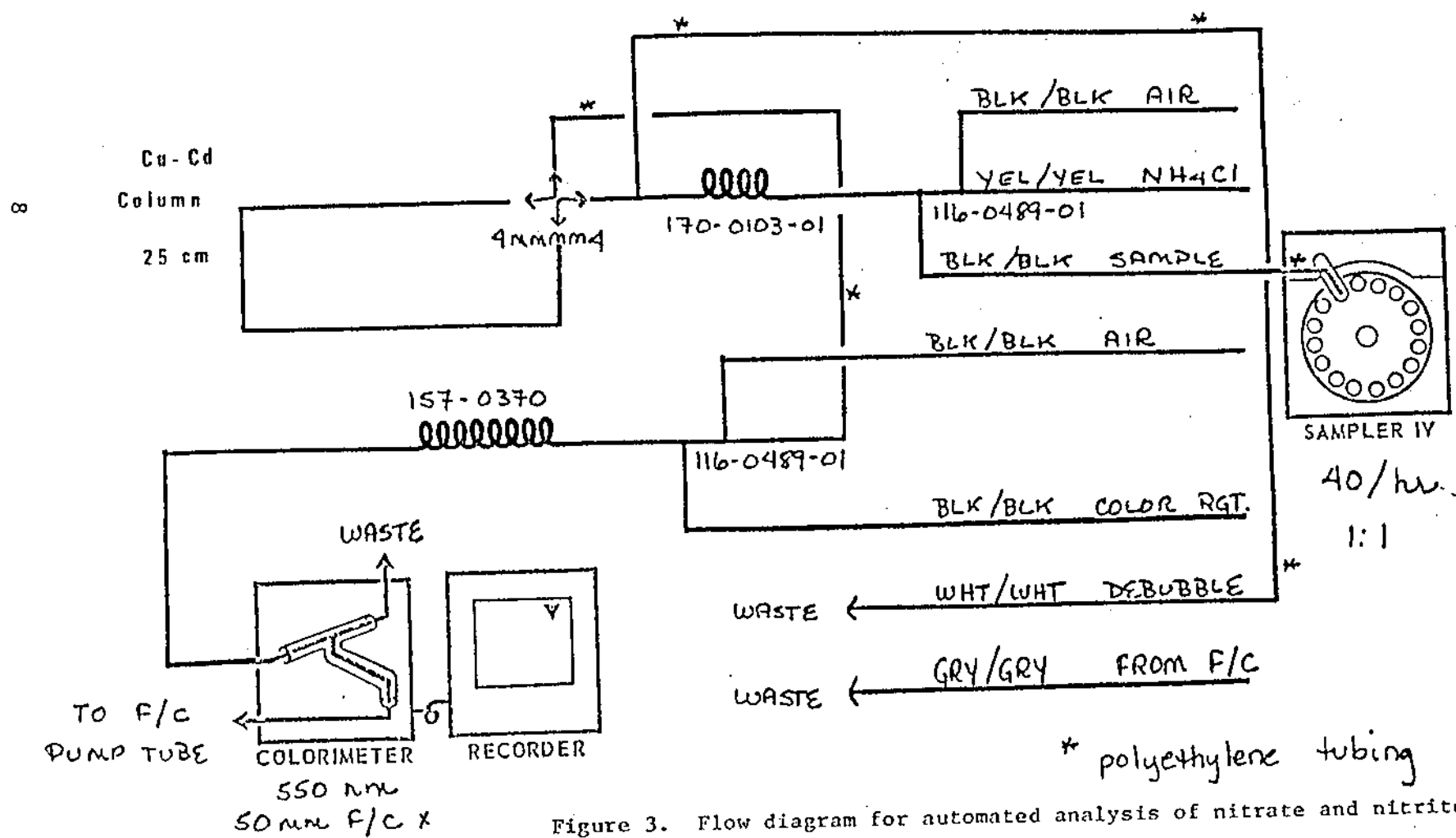


Figure 3. Flow diagram for automated analysis of nitrate and nitrite

II.

4. NITRITE

The basic method for this analysis is Technicon Industrial Method No. 161-71W, which is a modification of APHA (1977).

The only reagent utilized in the nitrite system is the color reagent, which is prepared exactly as described under the discussion of the nitrate + nitrite method. DDW is used in the preparation of this reagent, as Sampler IV wash water, and in setting AutoAnalyzer baseline. We find a reagent blank absorbance ranging from 0.02 to 0.04 using DDW as a sample.

The flow diagram for the nitrite system is shown in Figure 4.

Some operational notes for this method are summarized below:

- a) A phase separator (Technicon No. 021-G001-01) helps reduce noise by eliminating the inter-sample bubble which may tend to be a problem.
- b) A 40/hr 4:1 or 50/hr 6:1 cam gives good, reproducible results.
- c) The colorimeter phototubes must be S-10 (Technicon No. 199-B021-01).
- d) For routine analysis a STD CAL of 8.00 will give a full scale value of approximately 2 $\mu\text{g at/l}$.
- e) For a discussion of calibration and blank problems refer to Sections III 2-3.
- f) We have, in the past, had noise in this system due to "bubble-dip" in front of the flow cell when the pump phased just right with the bubble position. This problem was solved by replacing the white/white pull-through pump tube with an orange/orange, thereby reducing the rate of pull through.

NITRITE

116-D221-01

STD CAL 8.00

RANGE 0-2 μg at / l

SAMPLER IV ← GRN / GRN SAMPLER WATER
WASH

BLK / BLK AIR

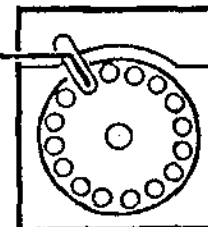
BLK / BLK AIR

ORN / ORN COLOR REAGENT

ORN / ORN SAMPLE *

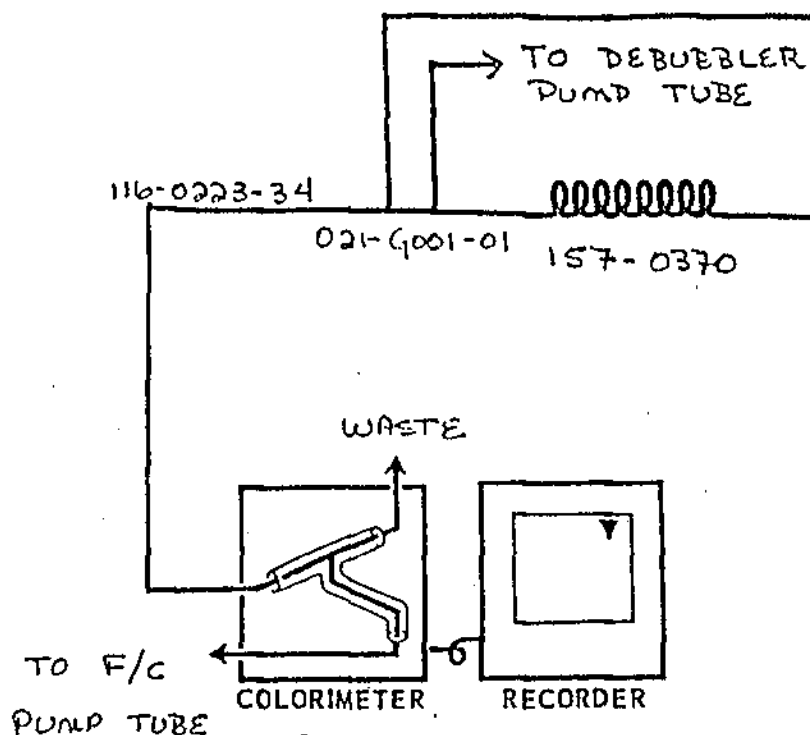
WASTE ← ORN / ORN FROM F/C

WASTE ← ORN / ORN DEBUBBLER



SAMPLER IV

50/hw
6:1



550 nm

50 mm F/C X

1.5 mm ID

*polyethylene tubing

Figure 4. Flow diagram for automated analysis of nitrite in seawater.

II.

5. AMMONIA

The method described here is that of O'Connor and Miloski (1974), with a few modifications. The basic method, however, was described by Grasshoff and Johannsen (1972).

Below are described the reagents used in the ammonia system. All reagents should be ACS grade; all water should be distilled and deionized (DDW). DDW is also used as Sampler IV wash water and in setting Auto-Analyzer baseline. We find a reagent blank absorbance ranging from 0.02 to 0.05 using DDW as a sample.

Buffer: Dissolve each of the following separately, then mix and dilute to 250 ml: 2.25 g boric acid, 30.0 g sodium citrate, and 0.5 g sodium hydroxide. Stable for a few weeks if refrigerated.

Reagent A: Dissolve 8.75 g phenol and 0.1 g sodium nitroprusside and make to 250 ml with DDW. Stable for a few weeks if refrigerated.

Reagent B: Dissolve 5 g sodium hydroxide and 0.5 g sodium dichloro-s-triazine-trione (sodium dichloro-isocyanurate) and make to 250 ml with DDW. Prepare fresh daily. This volume may be reduced depending on the amount needed for a set of samples. Consumption rate is 6 ml/hr.

Some operational notes for this method are summarized below:

- a) A phase separator (Technicon No. 021-G001-01) helps reduce noise by eliminating the inter-sample bubble which may tend to be a problem.
- b) A 40/hr 1:1 will give good, reproducible results.
- c) The colorimeter phototubes must be S-10 (Technicon No. 199-B021-01).
- d) For routine analysis a STD CAL of 8.00 will yield a full scale value of approximately 5 μg at/l.
- e) For a discussion of calibration and blank problems refer to Sections III 2-3.
- f) Smoking in the laboratory, and the use of ammonia-containing cleaning agents should be avoided to help reduce atmospheric contamination of ammonia.
- g) Segmented air supply should be scrubbed through concentrated H_2SO_4 to further avoid atmospheric contamination.

II.

5. AMMONIA (Continued)

- h) Plastic sample cups should be well rinsed (3-4 times) with the sample before use. They need not be acid washed.
- i) The sodium dichloro-s-triazine-trione may be purchased from the following supplier:

K & K Laboratories, Inc.
Plainview, New York

catalog no.: 17779

AMMONIA

116-D223-01 (MODIFIED)

STD CAL 8.00

RANGE 0.5 μg at/l

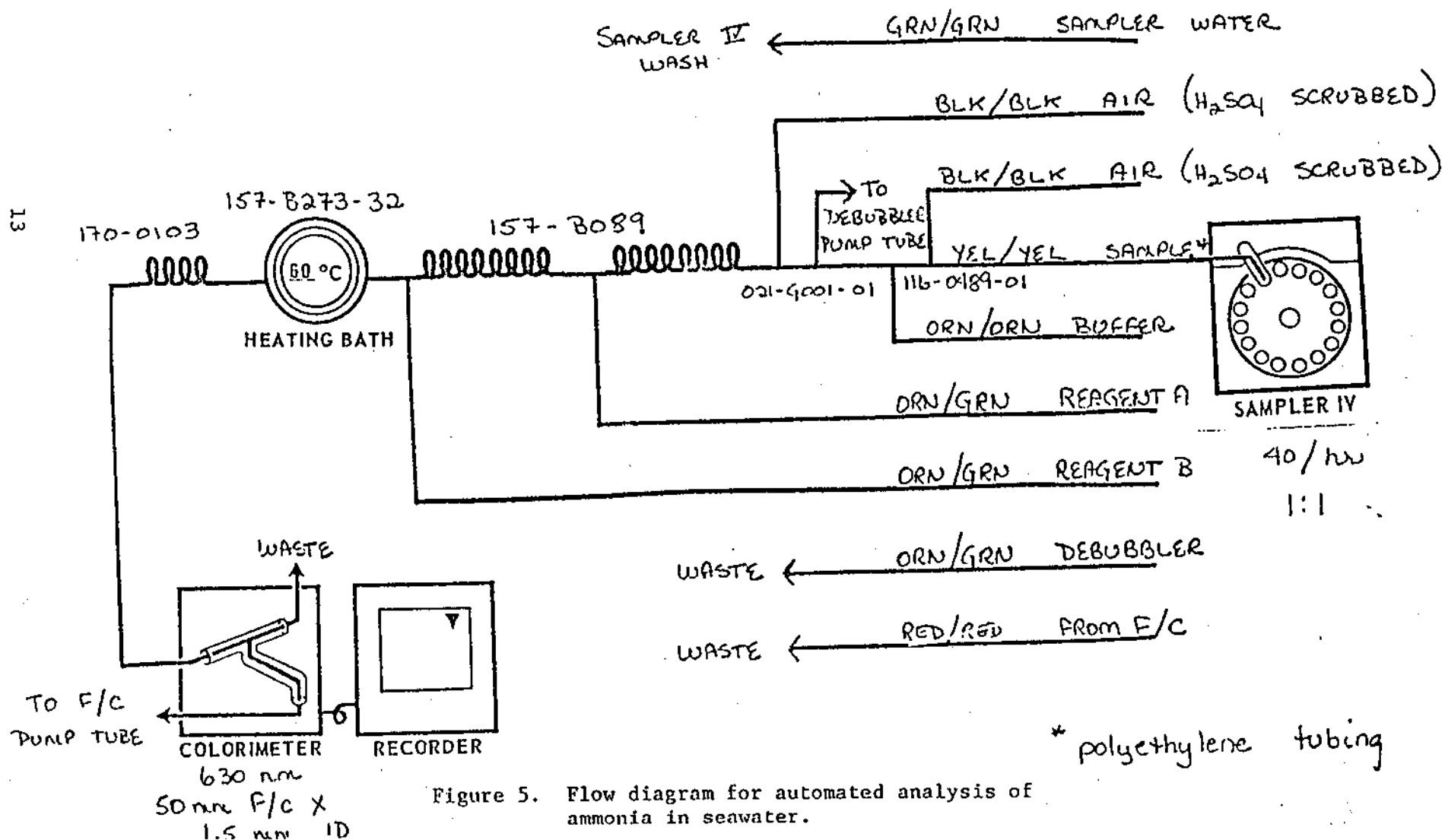


Figure 5. Flow diagram for automated analysis of ammonia in seawater.

III.

OPERATIONAL PROCEDURES

1. SET-UP

The following procedures should be followed every day the Auto-Analyzer is set up:

1. Colorimeters, heating baths and recorders should be turned on at least one hour before instrument calibration.
2. Pump DDW through all lines for 10-15 min. Use a separate water bottle for each chemistry and do not mix under any circumstances.
3. Wash for 5 min with 1N HCl or NaOH if necessary to establish a smooth bubble pattern. This will be particularly important for phosphate.
4. Rinse with DDW again for 5-10 minutes.
5. Set STD CAL on colorimeters to 1.00. Check zero and full scale. Establish a baseline with DDW in all lines (Sampler IV and reagents).
6. Begin pumping reagents with DDW from the Sampler IV.
7. Record the height of the reagent baseline. This should remain constant for fresh reagents; if not, it is a good indication that one of the reagents should be replaced.
8. Reset baseline. Turn STD CAL to approximate operating value.
9. Proceed with standards and calibration.

III.

2. STANDARDS AND CALIBRATION; SAMPLES

For routine operation one standard of approximately mid-scale value will be sufficient. The procedure for this will be discussed in detail below.

However, it is of utmost importance to check the system with several standards over a range of concentrations under the following circumstances:

1. each time the colorimeter has been aligned or "peaked".
2. whenever analyzing samples that are at the limit of the range of the method.
3. if the system has not been used for several months.
4. if the system has undergone a relocation. This is important when a system is moved from laboratory to shipboard and vice versa.

This type of check is important to establish the following information:

1. linearity of the system. This is frequently overlooked by many analysts, and consequently samples are analyzed above the Beer's Law range of the system, leading to erroneous values.
2. sample carry-over. Although it is recommended that all samples of a similar concentration be analyzed together, this is not always possible. Thus, it is extremely important to know whether low values will be contaminated by higher ones. If this effect is large, a different cam may solve the problem. The following series is recommended to determine linearity and sample carry-over. The numbers represent chart paper values, which correspond to an appropriate concentration of a standard.

<u>Sample cup #</u>	<u>Chart paper value</u>	
1	60	set calibration with these standards using STD CAL
2	60	
3	60	
4	20	
5	20	
6	40	
7	40	
8	60	
9	60	
10	80	
11	80	
12	100	
13	100	
14	20	
15	20	

III.

2. STANDARDS AND CALIBRATION; SAMPLES (Continued)

Samples number 2-13 will establish whether or not the system is responding linearly through that range of standards; samples number 13-15 will establish whether or not there is inter-sample contamination.

For routine operation samples should be analyzed in 40-sample batches (the capacity of a Sampler tray). Three standards of one concentration for each nutrient are placed at the beginning of the tray. The values for these standards should approximate the values of the samples. This standard is then adjusted to mid-scale using the STD CAL. This STD CAL value is recorded on the chart paper along with identification of the nutrient being analyzed, the date and the run number.

When running many trays in sequence allow 3-4 minutes of DDW baseline between trays to determine drift and reset the baseline if necessary. If you allow longer time between trays we recommend using 4 standards of each type at the start of a tray since the system must "coat up" and come to equilibrium with the nutrient being analyzed. Important to note: When setting up a sequence of samples on the tray, always run duplicates of the first sample after standards since a change in ionic strength (addition of seawater) always makes the first seawater sample 10-30% higher than it should be due to desorption problems. Use data from the second sample.

A typical data sheet is shown in Figure 7. On it there are appropriate spaces for identifying the sample (station number and depth), recording the peak height value from the chart paper, and recording intermediate and final concentration values. There is also a place to record baseline drift from that run. Calculations are discussed in more detail in section III - 5.

III.

3. BLANK AND SALINITY CORRECTIONS

The absorbance peak obtained by an automated system for a given nutrient in a seawater sample (when compared to a deionized distilled water baseline) represents the sum of absorbances from at least four sources (Fig. 8): 1) the light loss due to the differences in the index of refraction of the seawater and the deionized distilled water baseline; 2) reaction products (i.e. precipitates) of appropriate wetting agents and the seawater; 3) the absorbance of colored substances in the sample, either particulate or dissolved; and 4) reaction products of the nutrient in the sample and the color reagents. These reaction products may be variable due to a "salt error" caused by a shift in the position of equilibrium as a function of a change in the ionic strength of the solution (Brewer and Riley, 1965).

Loder and Glibert (1977) provide a full explanation of the rationale of applying such corrections to each nutrient; here we will just summarize the magnitude of such corrections, and methods for determining them.

The corrections for refractive index for each chemistry are given in Table I; the percent salt error relative to distilled deionized water standards for each chemistry is shown in Figure 9. These corrections are intended only as a guide to show the extent and type of correction necessary. It is important that individual analysts determine the appropriate corrections for their own system and methodology.

On a routine basis, Loder and Glibert (1977) suggest the following methods for determining the refraction and salt errors. In both methods DDW is used to set the baseline and as a wash between samples.

Method 1: Open ocean or narrow salinity range samples. Prepare standards with low nutrient natural seawater (NSW). Prepare standards in volumetric flasks using precision small volume auto-pipets; this way the standard addition does not significantly alter the salinity. Silicate standards must be prepared in polypropylene volumetrics to avoid leaching of silica from glass.

Analyze standards using normal reagents and run a blank on the water used to make the standards. Subtract the blank from the standards, and then determine the full scale value for that analysis.

Determine the refractive index correction for the samples by analyzing representative samples with only deionized water in the diluent lines and a reagent from which one of the color formers has been eliminated in the reagent lines. The concentration of the nutrient in the samples is then determined: $\text{corrected concentration} = [(\text{peak height of sample}) \cdot (\text{full scale value}) \div 100] - [\text{refractive index corr. in conc. units}]$.

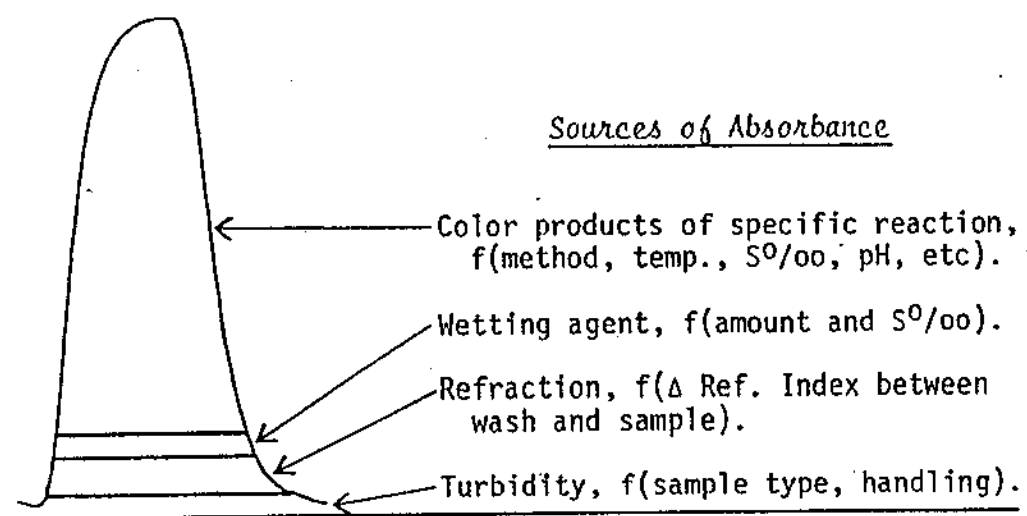


Figure 8. Sources of absorbance for a seawater nutrient sample.

Table I. Summary of Refractive Index (RI) corrections for methods discussed in text.

Method and Reference	STD CAL	Full Scale Value ($\mu\text{g at/l}$)	RI correction $f(S^{\circ}/_{\text{OO}})^{**}$ ($\mu\text{g at/l}$)
Phosphate (4)	8.00	5	0.006 ($S^{\circ}/_{\text{OO}}$)*
Silicate (2)	8.00	23	0.012 ($S^{\circ}/_{\text{OO}}$)
Nitrite (24)	7.70	2	0.0019 ($S^{\circ}/_{\text{OO}}$)
Nitrate (26)	8.00	7.6	0.0045 ($S^{\circ}/_{\text{OO}}$)
Ammonia (33)	8.00	5	0.0057 ($S^{\circ}/_{\text{OO}}$)

*Includes effect of Levor IV at 0.5 ml/l concentration in the diluent.

**These values can be approximated at different STD CAL settings if the dilution ratios remain the same. Multiply f by the ratio:full scale absorbance at STD CAL given above + full scale absorbance at new STD CAL.

III.

3. BLANK AND SALINITY CORRECTIONS (Continued)

Method 2: Estuarine or variable salinity samples. For samples with a wide range of salinities we suggest that routine standards be prepared in DDW and that a separately determined salt error factor be applied to the observed concentration to obtain the correct value.

We suggest the following procedure to determine the salt error correction value: Dilute low nutrient NSW with DDW to make a range of salinities. Prepare standard additions as described in Method 1 above, as well as DDW standards, using a precision small volume auto-pipet. Analyze the DDW standards and each dilution as well as the dilutions with the standard additions.

Determine the difference in concentrations between the seawater dilutions and those with the standard additions. Calculate the change in apparent nutrient concentration relative to the DDW standards as a function of salinity. Finally, to obtain the corrected concentration, subtract the appropriate refractive index correction, as described in Method 1, from the observed apparent concentration and multiply by the salt error factor.

III.

4. SHUT-DOWN

At the end of an operation day, the following procedures should be carried out:

1. Place all reagent lines in the DDW bottles specific for that analysis.
2. Return the sampler probe to the Sampler IV.
3. Pump DDW through the system for 10-15 minutes.
4. If system will not be set up the following day, then remove all reagent lines from DDW bottles and remove the sampler probe from sampler wash, and pump air through the system until all lines are dry.
5. Unplug heating baths.
6. Remove recorder pins, cap the tips, and turn recorder to off position.
7. Turn off colorimeters.
8. Remove pump platen and loosen pump tubes.

III.

5. DATA CALCULATIONS

Aspects of data calculations have been discussed in Sections III-2 and III-3; here the procedure will be summarized.

1. Peak heights for standards and samples are read and recorded on the data sheets as shown in Figure 7.
2. Baseline drift for the analysis set is read and also recorded on the same data sheet.
3. Full scale value for the data set is determined as follows:

$$\text{full scale value} = \frac{(\text{conc of std} - \text{conc of blk})}{(\text{pk ht of std} - \text{pk ht of blk})} \times 100$$

4. The concentration of each sample is then determined by using one of the following calculator programs which corrects each peak for the appropriate baseline drift and then determines the sample concentration based on the full scale value determined above. Program 1 is algebraic. It was written for a Texas Instruments 56, but could easily be adapted to any algebraic calculator. Program 2 was written in reverse Polish notation for a Hewlett-Packard 55. The algebraic program has an option to subtract a refractive index correction and multiply by a salt correction factor. It is important that the analyst be aware of which corrections must be applied to which chemistries and the magnitude of such corrections.

IV. SENSITIVITY AND REPRODUCIBILITY OF AUTOMATED ANALYSES

Hager et al. (1972) summarize, what quality data from an automated system depends on:

"As the literature indicates, the quality of the results is usually more dependent on the operator than the method - a point well appreciated by seagoing scientists"

Instrumental variability and replicate sampling variability were determined for very low level analyses at the University of New Hampshire laboratory (Glibert and Loder, in prep.). In order to determine instrumental variability, four 500 ml samples were analyzed approximately 9 to 10 times throughout a day. The standard deviations and percent variations were calculated for each nutrient (Table II). Nitrite proved to have the highest variability (2.6%).

Replicate sampling variability was determined by collecting six sets of quintuplicate samples. These samples were then analyzed during the same time period (to minimize machine drift), and the average standard deviation and percent variation were calculated (Table II). Only in the case of silicate was the replicate sampling variability higher than the analytical variability. There is evidence that this high silicate sampling variability may have been due to planktonic or sedimentological contamination, but this is uncertain.

Table II. Analytical and replicate sampling variability for nutrient samples.

parameter (units)	salinity (‰)	NO ₂ -N (µg at/l)	NO ₃ -N (µg at/l)	PO ₄ -P (µg at/l)	SiO ₂ -S (µg at/l)
range of method	0-40	0-2	0-5	0-5	
range of sample conc.	28-30	0.1-0.4	0.1-1.0	1.0-2.0	4.0-7.0
analytical variability ^a	-	0.009 (2.6%)	0.05 (1.2%)	0.02 (1.7%)	0.08 (1.4%)
replicate sampling variability ^b	0.003 (0.01%)	0.002 (0.7%)	0.04 (0.8%)	0.01 (1.0%)	0.43 (6.4%)

^a Based on the average standard deviations of 9-10 replicate runs of the same samples.

^b Based on the average standard deviations of numerous sets of replicate samples run at the same time.

VII.

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APPENDIX II: RECOMMENDED SAMPLE COLLECTION AND STORAGE PROCEDURES

It is well known that variability or error can be introduced to a sample from: the type of storage container, chemical preservation, filtering, the temperature of storage, and the length of time samples have been stored. No single storage method will be suitable for all water types, or for all seasons. As a guideline, the following is suggested:

1. Type of bottle. High density linear polyethylene or polycarbonate is superior to soft polyethylene.
2. Pretreatment of bottle. Rinse a clean bottle with acid (10% HCl), then distilled deionized water, then several times with the sample.
3. Chemical preservation. No preservative is necessary for open ocean samples if immediately frozen. A preservative should be used if samples have a high organic content. HgCl₂ (of final concentration in sample of ~100 ppm) is recommended for nitrate, nitrite, phosphate and silicate. We use 0.5 ml of a 2% w/v solution added to a 100 ml sample. HgCl₂ should be avoided in preserving ammonia; instead a phenol-alcohol mixture is recommended. (Dissolve 10g phenol in 100 ml of 95% v/v ethyl alcohol USP. Add 2 ml phenol solution to 50 ml sample.)
4. Means of storage. Samples should be immediately frozen if possible. Allow plenty of air space at top of bottle (at least 1.5 cm) for expansion. Caps should be very tight. Keep samples upright until fully frozen, to avoid leakage through cap. Tighten caps again after samples are frozen.
5. Filtration. Depends on samples. Millipore filters may contaminate ammonia and phosphate; glass fiber filters may contaminate silicate.
6. Length of storage time. Samples should be analyzed as soon after collection as possible. Significant changes will occur in ammonia, even if a preservative is used.

The above is meant merely as a guideline. For more exhaustive treatments of the subject, the reader is referred to the articles listed on the next page.

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APPENDIX B

SUMMARY OF THE Hg RESULTS FOR SAMPLES
COLLECTED DURING THE JULY 1988
NEW YORK BIGHT SURVEY

TABLE B-1. CORRECTED Hg RESULTS FOR SAMPLES COLLECTED DURING THE NEW YORK BIGHT SURVEY (JULY 1988).

Station	Depth 1 ^a	Depth 2 ^b	Batch	Hg ^c (g/L)
A2	11.4	17.1	1	1.515
A4	7.6	34.3	1	4.616
A6	13.3	66.6	1	0.248
A8	9.5	95.2	2	2.768
A10 ^d	9.5	104.7	1, 4 ^e	3.536
A11	13.3	104.7	1	1.648
A13	7.6	55.2	1	3.295
A15	7.6	38.1	1	1.264
B2	5.7	15.2	2	1.441
B4	9.5	40.0	2	3.245
B5	9.5	32.4	2	0.826
B6	9.5	28.6	2	0.982
B8	7.6	24.7	2	0.539
B10	3.8	17.1	2	2.110
C1	5.7	15.2	3	11.376
C2	5.7	13.3	3	13.250
C3 ^d	5.7	20.9	4 ^e	6.220
C3 ^d	5.7	20.9	4 ^e	6.644
C4	5.0	15.2	4 ^e	49.759
C5	5.7	15.2	3	9.782
C6	3.8	13.0	3	10.061
C7	3.0	7.6	3	6.329
C8	3.0	15.0	3	7.392
C10	3.0	10.0	3	4.978
C11	5.0	15.0	4 ^e	6.316
C13	5.0	35.0	4 ^e	2.484
C15	5.0	20.0	2	1.089
Field Blank			1	f

^aSurface depth.

^bPycnocline depth.

^cSamples were pooled from surface and pycnocline depths; 1/2 from each depth.

^dMean value.

^eBatch 4 samples analyzed on 2 days designated A and B.

^fThe field blank was determined to contain less mercury than the procedural blank

**TABLE B-2. QUALITY CONTROL DATA FOR Hg SAMPLES:
REPLICATES**

Sample No.	Measured Concentration (ng Hg/L)
GG89-HG-1-1	5.088
GG89-HG-1-2	7.351
Mean	6.220
Percent RPD	36
GG89-HG-2-1	5.608
GG89-HG-2-2	7.680
Mean	6.644
Percent RPD	31

TABLE B-3. QUALITY CONTROL DATA FOR Hg SAMPLES:
BLANK SPIKING EXERCISE

Batch No.	Sample No.	Hg Measured (in ng)	Hg Added (in ng)	Percent Recovery
Batch 1	GH68-BS	2.549	4.08	62
	GH69-BS	3.413	-	84
Batch 2	GH74-BS	1.718	4.08	42
	GH75-BS	2.323	-	57
Batch 3	GH90-BS	2.575	4.08	63
	GH91-BS	2.810	-	69
Batch 4A	GI03-BS	1.871	-	46
	GI04-BS	2.292	-	56
Batch 4B	GI05-BS	2.166	4.08	53
	GI06-BS	4.322	-	106

TABLE B-4. QUALITY CONTROL DATA FOR Hg SAMPLES: MATRIX SPIKING EXERCISE.

Sample No.	Measured Concentration (ng Hg/L)	Expected Concentration of Hg (ng Hg/L)	Hg Added (ng)	Percent Recovery
GG89-HG-1	16.275	22.22	4.08	73
GG89-HG-2	12.248	22.964	-	53

APPENDIX C

SUMMARY OF TRACE METALS DATA
(EXCLUDING Hg) FOR SAMPLES
COLLECTED DURING THE JULY 1988
NEW YORK BIGHT SURVEY

TABLE C-1. SUMMARY OF ACID SOLUBLE TOTAL TRACE METAL CONCENTRATIONS FOR SAMPLES COLLECTED DURING THE JULY 1988 NEW YORK BIGHT SURVEY. RESULTS ARE IN μg OF METAL/L OF SEAWATER. FIELD REPLICATES ARE DESIGNATED WITH PARENTHESES.

Station	Depth	Cd	Cu	Fe	Ni	Pb	Zn
A2(1)	11.4	0.026	0.32	4.05	0.36	0.033	0.55
A2(2)	11.4	0.028	0.32	3.73	0.39	0.024	0.60
A2(1)	17.1	0.023	0.28	2.73	0.33	0.021	0.43
A2(2)	17.1	0.024	0.26	2.57	0.32	0.021	0.36
A4a	7.6	0.025	0.48	5.69	0.48	0.061	1.42
A4	34.3	0.024	0.19	2.85	0.28	0.022	0.30
A6	13.3	0.010	0.14	0.55	0.21	0.054	0.39
A6	66.6	0.018	0.12	1.02	0.23	0.017	0.14
A8	9.5	0.017	0.19	0.34	0.26	0.020	0.18
A8	95.2	0.015	0.07	0.30	0.29	0.015	4.44
A10	9.5	0.020	0.21	0.42	0.29	0.029	0.15
A10	104.7	0.017	0.09	1.49	0.20	0.017	0.23
A11	13.3	0.017	0.13	0.40	0.25	0.018	0.07
A11	104.7	0.019	0.09	3.41	0.23	0.027	0.09
A13(1)	7.6	0.022	0.20	0.46	0.32	0.028	0.20
A13(2)	7.6	0.021	0.19	0.40	0.31	0.022	0.28
A13(1)	55.2	0.020	0.13	2.10	0.28	0.067	0.11
A13(2)	55.2	0.022	0.15	2.24	0.35	0.019	0.17
A15	7.6	0.024	0.24	1.86	0.32	0.020	0.22
A15	38.1	0.027	0.18	7.53	0.29	0.021	0.24
B10(1)	3.8	0.033	0.56	3.19	0.48	0.044	1.12
B10(2)	3.8	0.038	0.63	3.79	0.55	0.052	1.30
B10(1)	17.1	0.034	0.59	47.9	0.44	0.200	1.31
B10(2)	17.1	0.033	0.58	46.7	0.43	0.200	1.30
B8	7.6	0.030	0.43	4.75	0.38	0.041	0.71
B8	25.8	0.032	0.47	4.70	0.37	0.041	1.11
B6a	9.5	0.029	0.45	0.65	0.38	0.022	0.53
B6	28.6	0.031	0.32	3.11	0.30	0.026	0.61
B5	9.5	0.030	0.48	0.95	0.42	0.023	0.58
B5	32.5	0.029	0.34	5.65	0.33	0.033	0.77
B4(1)	9.5	0.031	0.50	1.44	0.44	0.027	0.75
B4(2)	9.5	0.033	0.52	1.49	0.42	0.028	0.81
B4(1)	40.0	0.044	0.56	30.6	0.39	0.238	1.64
B4(1)	40.0	0.043	0.53	33.0	0.38	0.239	1.63
B2	5.7	0.044	0.76	7.4	0.64	0.086	1.93
B2	15.2	0.049	0.75	34.7	0.48	0.289	3.11
C15	5.0	0.040	0.64	4.0	0.54	0.045	1.70
C15	20.0	0.034	0.39	5.5	0.35	0.040	1.20
C13(1)	5.0	0.055	0.91	17.0	0.81	0.179	3.12
C13(2)	5.0	0.051	1.04	22.7	0.88	0.212	2.87
C13(1)	35.0	0.048	0.74	49.7	0.42	0.437	2.82
C13(2)	35.0	0.051	0.80	58.1	0.43	0.485	2.37
C11	5.0	0.065	1.29	57.4	0.99	0.466	4.22
C11	15.0	0.038	1.03	46.2	0.45	0.345	2.60

TABLE C-1. (Continued)

Station	Depth	Cd	Cu	Fe	Ni	Pb	Zn
C10	3.0	0.070	1.83	100.0	1.44	0.863	9.28
C10	10.0	0.066	1.43	95.2	0.87	0.704	5.31
C8	3.0	0.067	1.78	81.5	1.46	0.825	6.86
C8	15.0	0.047	1.36	70.1	0.91	0.549	5.21
C7	3.0	0.087	2.33	95.2	1.90	0.867	8.42
C7	7.6	0.077	2.33	97.9	1.84	0.855	8.18
C6	3.8	0.063	1.79	84.5	1.51	0.801	6.52
C6	13.0	0.055	1.49	78.2	1.21	0.656	4.70
C5	5.7	0.082	2.42	147.9	2.02	1.39	7.23
C5	15.2	0.064	2.05	135.5	1.47	1.11	5.76
C4	5.0	0.104	3.30	228.1	2.46	1.96	9.42
C4	15.2	0.068	2.27	194.8	1.46	1.35	4.83
C3(1)	5.7	0.090	2.70	180.8	2.24	1.57	9.63
C3(2)	5.7	0.088	2.81	187.8	2.33	1.70	10.08
C3(1)	20.9	0.075	2.46	184.0	1.87	1.40	6.21
C3(2)	20.9	0.074	2.46	187.2	1.76	1.46	6.51
C2	5.7	0.109	4.44	207.6	2.60	1.86	9.25
C2 ^a	13.3	0.121	3.77	345.0	2.40	2.96	18.77
C1	5.7	0.104	3.36	268.4	2.58	2.01	9.38
C1	15.2	0.093	2.96	223.0	2.37	1.72	9.13
Bottle Blank		ND	0.012	0.11	<0.02	<0.003	0.03

ND = Not detectable.

^aMean of duplicates.

TABLE C-2. RESULTS OF ANALYSIS OF DUPLICATE SAMPLE EXTRACTIONS. RESULTS ARE IN μg OF METAL/L OF SEAWATER. MEAN AND RELATIVE PERCENT DIFFERENCE (PERCENT RPD) REPORTED FOR EACH SET OF DUPLICATE ANALYSES.

Sample	Depth (m)	Cd	Cu	Fe	Ni	Pb	Zn
A4(1)	7.6	0.022	0.40	5.69	0.38	0.56	1.37
A4(2)	7.6	0.028	0.55	5.68	0.58	0.67	1.46
Mean		0.025	0.48	5.69	0.48	0.61	1.42
Percent RPD		24	32	0	42	18	6
B6(1)	9.5	0.030	0.46	0.71	0.39	0.024	0.55
B6(2)	9.5	0.029	0.43	0.59	0.37	0.020	0.50
Mean		0.029	0.45	0.65	0.38	0.022	0.53
Percent RPD		3	7	18	5	18	10
C2(1)	13.3	0.120	3.75	347.3	2.40	2.87	18.71
C2(2)	13.3	0.122	3.80	342.7	2.41	2.92	18.82
Mean		0.121	3.77	345.0	2.40	2.90	18.77
Percent RPD		2	1	1	0	2	1

TABLE C-3. SUMMARY OF THE RECOVERY OF METALS FROM CANADIAN STANDARD REFERENCE SEAWATER CASS-1 PROCESSED AND ANALYZED WITH SAMPLES. CONCENTRATIONS ARE IN $\mu\text{g/L}$ AND RECOVERY IN PERCENT (% R).

Sample	Cd	%R	Cu	%R	Fe	%R
Expected	0.026		0.291		0.873	
1	0.026	100	0.34	117	1.03	118
2	0.022	85	0.29	100	0.87	100
3	0.020	77	0.31	107	0.74	85
4	0.023	88	0.33	113	0.72	82
5	0.019	73	0.31	107	0.70	80
6	0.022	85	0.33	113	0.82	94
Mean	0.022	85	0.32	109	0.81	93
	Ni	%R	Pb	%R	Zn	%R
Expected	0.290		0.251		0.980	
1	0.39	134	0.209	83	1.14	116
2	0.37	128	0.231	92	1.05	107
3	0.29	100	0.222	88	1.58	161
4	0.30	103	0.233	93	1.09	111
5	0.30	103	0.215	86	0.95	97
6	0.32	110	0.235	94	1.06	108
Mean	0.33	113	0.224	89	1.15	117

TABLE C-4. SUMMARY OF THE SPIKING MATERIALS RECOVERY OF METAL ADDED TO SAMPLES DURING PROCESSING OF WATER SAMPLES. THE AMOUNT OF METAL FOUND, THE EXPECTED AMOUNT, AND THE PERCENT RECOVERY (%R) OF THE KNOWN ADDITION ARE SHOWN.

Sample	Found (ng)	Expected (ng)	%R	Found (ng)	Expected (ng)	%R
Cd				Cu		
A4 7.6 m	17.0	25.4	67	101.8	120.3	85
B6 9.5 m	28.6	26.0	110	116.0	110.3	105
C2 13.3 m	44.6	44.9	99	804	789	102
Fe				Ni		
A4 7.6 m	1292	1262	102	136	148	92
B6 9.5 m	253	228	111	128	124	103
C2 13.3 m	74360	70267	106	554	538	103
Pb				Zn		
A4 7.6 m	32.3	36.6	88	323	357	90
B6 9.5 m	27.2	28.4	96	181	171	106
C2 13.3 m	622	614	101	3939	3885	101

APPENDIX D

SUMMARY OF THE NUTRIENT RESULTS
FOR SAMPLES COLLECTED DURING THE JULY 1988
NEW YORK BIGHT SURVEY

TABLE D-1. SUMMARY OF TOTAL AND DISSOLVED NUTRIENT DATA (IN μM OF NUTRIENT/L OF SEAWATER) FOR SAMPLES COLLECTED DURING THE NEW YORK BIGHT SURVEY (JULY 1988).

Station	Rep ^a	Depth	NH ₄ ^b	NO ₃ ^b	NO ₂	PO ₄ ^b	SiO ₄	TOT N	TOT P
A-1	1	3.8	2.15	2.35	0.04	0.23	3.00	-	-
	2 ^c	-	0.24	7.05	0.03	0.26	3.48	-	-
	3	-	0.02	0.27	-	0.35	-	14.6	0.79
	1	11.4	3.78	358 ^d	0.18	0.31	3.46	-	-
	2 ^c	-	0.45	361 ^d	0.18	0.30	3.50	-	-
	3	-	3.24	0.45	-	0.29	-	14.3	0.73
A-2	1	11.4	0.10	21.2 ^d	0.03	0.28	3.98	-	-
	3	-	1.38	0.28	-	0.27	-	17.9	0.70
	1	17.1	0.71	52.7	0.07	0.31	3.72	-	-
	3	-	9.73	0.28	-	0.31	-	69.8	0.72
	1	9.5	0.10	7.92	0.05	0.18	1.71	-	-
	3	-	ND	0.31	-	0.12	-	65.3	0.43
A-3	1	34.2	1.34	19.1	0.07	0.35	4.20	-	-
	3	-	NA	NA	-	NA	-	1802	0.97
	1	7.6	23.6 ^d	350 ^b	0.04	0.14	1.21	-	-
	3	-	4.50	36.5 ^d	-	0.10	-	14.1	0.20
	1	34.3	5.21 ^d	60.6 ^d	0.10	0.40	3.95	-	-
	3	-	4.85	31.8	-	0.36	-	36.4	0.83
A-4	1	7.6	104 ^d	69.5 ^d	0.06	0.43	2.73	-	-
	2 ^c	-	0.16	24.6 ^d	0.03	0.48	2.33	-	-
	3	-	1.13	4.52	-	0.45	-	11.3	0.76
	1	41.9	17.3	399 ^d	0.15	0.56	2.54	-	-
	2 ^c	-	0.70	137	0.12	0.56	2.02	-	-
	3	-	ND	67.5	-	0.07	-	171	0.71
A-6	1	13.3	9.96 ^d	112 ^d	0.04	0.12	1.52	-	-
	3	-	ND	0.2	-	0.07	-	8.97	0.36
	1	66.6	0.72	65.4 ^d	0.15	0.73	5.31	-	-
	3	-	0.37	7.28	-	0.58	-	17.8	0.88

TABLE D-1. (CONTINUED).

STATION	REP ^A	DEPTH	NH ₄ ^B	NO ₃ ^B	NO ₂	P ₄ ^B	SIO ₄	TOT N	TOT P
A-7	1	3.8	0.04	1.3	ND	0.09	1.47	-	-
	3	-	ND	0.14	-	0.09	-	10.3	0.49
	1	62.8	1.69	18.6 ^d	0.38	0.69	5.31	-	-
	3	-	0.39	7.18	-	0.75	-	15.6	1.16
A-8	1	9.5	0.21	10.7	0.08	0.21	1.64	-	-
	3	-	NA	83.1	-	NA	-	669	0.43
	1	95.2	0.79	115 ^d	0.17	0.79	5.80	-	-
	3	-	ND	14.9	-	0.88	-	22.4	1.27
A-9	1	9.5	0.06	5.95	0.07	0.19	2.16	-	-
	3	-	ND	0.5	-	0.32	-	9.12	0.48
	1	81.9	7.26	13.7	0.09	0.57	4.38	-	-
	3	-	ND	8.22	-	1.13	-	16.1	0.78
A-10	1	9.5	0.13	67.1 ^d	0.11	0.21	2.29	-	-
	2 ^c	-	43.9 ^d	51 ^d	0.22	0.23	2.66	-	-
	3	-	0.24	1.12	-	0.14	-	8.98	0.49
	1	104.7	0.30	17.3 ^d	0.14	0.70	6.02	-	-
	2 ^c	-	0.29	15.0	0.12	0.72	5.94	-	-
	3	-	ND	13.2	-	0.58	-	16.9	0.82
A-11	1	13.3	0.14	0.57	0.15	0.24	2.17	-	-
	3	-	2.39	0.19	-	0.11	-	8.59	0.36
	1	104.7	21.9	1136 ^d	0.16	0.69	7.66	-	-
	3	-	NA	11.9	-	NA	-	662	0.85
A-12	1	15.2	0.08	31.1 ^d	0.14	0.23	2.04	-	-
	3	-	0.58	4.18	-	0.15	-	11.8	0.47
	1	60.9	0.02	14.8	0.10	0.55	5.36	-	-
	3	-	ND	7.36	-	0.46	-	15.0	0.78
A-13	1	7.6	0.04	0.86	0.11	0.22	2.22	-	-
	3	-	0.04	0.81	-	0.15	-	15.2	0.50
	1	55.2	6.55	260 ^d	0.61	0.68	5.57	-	-
	3	-	NA	>118	-	NA	-	163	0.87

TABLE D-1. (Continued).

Station	Rep ^a	Depth	NH ₄ ^b	NO ₃ ^b	NO ₂	PO ₄ ^b	SiO ₄	Tot N	Tot P
A-14	1	9.5	0.10	0.18	0.10	0.17	3.17	-	-
	3	-	ND	0.09	-	0.13	-	11.1	0.55
	1	51.4	2.84	9.27	0.69	1.92	9.13	-	-
	3	-	5.94	12.8	-	0.74	-	24.1	1.07
A-15	1	7.6	3.12	24.9 ^d	0.09	0.39	3.67	-	-
	3	-	ND	0.04	-	0.15	-	11.8	0.59
	1	38.1	4.26	2.15	0.15	0.95	14.5	-	-
	3	-	NA	85.6	-	NA	-	949	1.14
A-16	1	7.6	0.65	0.93	0.07	0.68	10.0	-	-
	3	-	6.65	19.0	-	0.42	-	25.5	1.16
	1	22.8	1.58	21.1	0.13	0.50	9.62	-	-
	3	-	ND	0.2	-	0.38	-	29.3	0.92
B-2	1	5.7	0.84	10.8	0.06	0.59	2.89	-	-
	3	-	0.35	0.4	-	0.48	-	19.0	1.37
	1	15.2	6.17	15.8	0.20	1.22	11.8	-	-
	3	-	-	75.4	-	-	-	324	1.60
B-3	1	2.5	2.36	16.3	0.07	0.54	2.90	-	-
	3	-	0.08	0.43	-	0.18	-	17.4	1.00
	1	28.6	1.24	0.69	0.12	0.88	9.18	-	-
	3	-	2.01	1.62	-	0.68	-	16.0	1.33
B-4	1	9.5	0.21	0.23	0.06	0.15	1.62	-	-
	3	-	1.75	3.04	-	0.09	-	25.2	0.69
	1	40	1.86	2.08	0.18	0.87	9.88	-	-
	3	-	13.9	>15.1	-	0.77	-	54.4	1.24
B-5	1	9.5	73.7 ^d	348 ^d	0.17	0.26	1.74	-	-
	2 ^c	9.5	0.34	13.5	0.07	0.43	0.95	-	-
	3	-	0.32	4.54	-	ND	-	17.1	0.60
	1	32.5	3.75	34.3 ^d	0.13	0.52	5.50	-	-
	2 ^c	32.5	1.10	1.06	0.11	0.52	4.67	-	-
	3	-	2.07	2.77	-	0.28	-	13.9	0.80

TABLE D-1. (Continued).

Station	Rep ^a	Depth	NH ₄ ^b	NO ₃ ^b	NO ₂	PO ₄ ^b	SiO ₄	Tot N	Tot P
B-6	1	9.5	0.04	0.07	0.06	0.21	1.01	-	-
	3	-	20.6	>24.3	-	0.02	-	362	0.51
	1	28.6	0.57	0.89	0.10	0.38	4.43	-	-
	3	-	2.07	<4.88	-	0.20	-	78.8	0.96
B-7	1	7.6	0.53	0.09	0.07	0.15	1.05	-	-
	3	-	ND	0.29	-	0.02	-	10.6	0.52
	1	24.7	0.67	0.51	0.16	0.62	6.11	-	-
	3	-	0.95	0.92	-	0.42	-	17.4	0.9
B-8	1	7.6	0.57	0.32	0.13	0.34	2.96	-	-
	3	-	0.07	0.39	-	0.15	-	13.5	0.73
	1	24.7	0.04	0.16	0.07	0.30	3.45	-	-
	3	-	0.75	1.23	-	0.13	-	16.0	0.73
B-9	1	7.6	2.48	7.15	0.07	1.06	2.06	-	-
	3	-	0.04	0.24	-	0.07	-	13.9	0.66
	1	22.8	0.56	10.9	0.08	0.56	5.14	-	-
	3	-	0.04	0.72	-	0.22	-	13.8	0.89
B-10	1	3.8	0.05	0.3	0.10	0.32	0.90	-	-
	3	-	ND	0.49	-	0.10	-	14.9	0.86
	1	17.1	0.22	1.92	0.07	1.50	8.34	-	-
	3	-	0.31	0.12	-	0.75	-	16.9	1.44
B-11	1	3.8	0.47	0.33	0.07	0.53	3.23	-	-
	3	-	ND	0.09	-	0.21	-	14.9	1.07
	1	15.2	1.30	1.07	0.17	1.70	9.48	-	-
	3	-	0.55	0.72	-	0.79	-	15.5	1.44
B-12	1	1.9	0.15	0.22	0.06	0.48	5.13	-	-
	2 ^c	-	0.15	0.08	0.06	0.30	4.28	-	-
	3	-	0.22	0.36	-	0.28	-	14.9	1.16
	1	7.6	0.33	0.25	0.05	0.73	8.05	-	-
	2 ^c	-	0.22	0.08	0.06	0.67	8.18	-	-
	3	-	2.39	0.89	-	0.49	-	42.7	1.63

TABLE D-1. (Continued).

Station	Rep ^a	Depth	NH ₄ ^b	NO ₃ ^b	NO ₂	PO ₄ ^b	SiO ₄	Tot N	Tot P
C-1	1	5.7	26.5	16.7	2.74	3.01	13.0	-	-
	3	-	>20.6	15.6	-	2.91	-	71.3	4.53
	1	15.2	25.3	15	2.40	3.14	13.7	-	-
	3	-	>24.0	14.2	-	2.78	-	61.9	4.05
C-2	1	5.7	29.0	16.4	2.69	3.45	13.7	-	-
	3	-	>20.0	15.1	-	2.82	-	66.8	4.12
	1	13.3	24.1	12.14	0.09	3.54	13.1	-	-
	3	-	>22.0	11	-	3.57	-	57.4	4.40
C-3	1	5.7	23.7	12.5	2.14	2.79	12.5	-	-
	3	-	>20.0	14.9	-	3.64	-	86.4	4.12
	1	20.9	14.9	8.71	1.40	2.31	9.96	-	-
	3	-	13.7	8.24	-	2.03	-	43.7	3.18
C-4	1	5	28.6	14.5	2.50	3.00	12.9	-	-
	3	-	>20.6	12.3	-	2.22	-	55.2	3.38
	1	15.2	10.6	6.38	1.02	1.67	8.97	-	-
	3	-	<9.58	<8.03	-	1.47	-	35.5	2.82
C-5	1	5.7	17.4	11.2	1.89	2.42	10.7	-	-
	3	-	19.7	13.7	-	3.23	-	53.3	3.49
	1	15.2	11.1	7.89	1.06	1.95	8.66	-	-
	3	-	10.6	6.63	-	1.68	-	36.5	2.76
C-6	1	3.8	13.9	10.4	1.02	1.83	7.07	-	-
	3	-	11.7	6.8	-	1.88	-	43.6	3.16
	1	13	6.75	4.55	0.71	1.44	7.78	-	-
	3	-	6.02	4	-	1.17	-	31.1	2.34
C-7	1	3	11.1	34.1	0.89	2.00	11.6	-	-
	3	-	7.70	5.23	-	2.14	-	40.8	3.79
	1	7.6	8.48	5.75	0.84	2.08	12.0	-	-
	3	-	8.23	5.28	-	2.05	-	41.9	3.75

TABLE D-1. (Continued).

Station	Rep ^a	Depth	NH ₄ ^b	NO ₃ ^b	NO ₂	PO ₄ ^b	SiO ₄	Tot N	Tot P
C-8	1	3	10.1	7.72	1.24	1.83	8.93	-	-
	2 ^c	-	10.1	7.15	1.21	2.66	8.70	-	-
	3	-	18.6	>24.3	-	1.75	-	99.7	2.94
	1	15	5.03	3.15	0.45	0.96	5.47	-	-
	2 ^c	-	4.29	3.49	0.37	1.34	6.63	-	-
	3	-	4.37	6.84	-	0.89	-	25.9	2.02
C-10	1	3	5.00	4.18	0.65	1.85	8.87	-	-
	3	-	7.62	5.44	-	1.55	-	36.3	2.81
	1	10	2.13	3.08	0.21	1.01	7.71	-	-
	3	-	1.89	1.32	-	0.86	-	22.0	1.92
C-11	1	5	1.76	1.49	0.23	1.13	7.45	-	-
	3	-	2.03	1.23	-	1.05	-	23.0	2.18
	1	15	0.11	0.4	0.07	0.94	7.68	-	-
	3	-	0.08	0.35	-	1.03	-	15.0	1.44
C-13	1	5	0.74	2.22	0.16	0.53	3.59	-	-
	3	-	ND	0.2	-	0.41	-	17.5	1.53
	1	35	1.54	1.48	0.14	0.84	8.76	-	-
	3	-	1.46	1.03	-	0.53	-	14.1	1.24
C-15	1	5	2.69	3.83	0.07	0.22	2.52	-	-
	3	-	20.7	>24.3	-	0.10	-	493	0.60
	1	20	0.05	0.2	0.12	0.60	5.77	-	-
	3	-	3.74	17.6	-	0.36	-	20.2	1.22

NA = Not analyzed; ND = Not detected.

> = Greater than; < = Less than.

^aReplicates 1 and 2 at each station are filtered and represent dissolved nutrient data. Replicate 3 at each station is not filtered and represents total nutrient data.

^bAnalysis of unfiltered samples (Rep 3) for NH₄, NO₃, and PO₄ was not originally planned, but because contamination was evident in the NO₃ data, these parameters were analyzed.

^cReplicate 2 was collected at all stations, but only analyzed for selected stations.

^dContamination suspected.

